

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
29 April 2004 (29.04.2004)

PCT

(10) International Publication Number  
**WO 2004/035700 A1**

(51) International Patent Classification<sup>7</sup>: **C09D 11/00**,  
C09B 47/24

(74) Agents: MORPETH, Fraser, Forrest et al.; Avecia Limited, Intellectual Property Group, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).

(21) International Application Number:  
PCT/GB2003/004023

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:  
19 September 2003 (19.09.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0223819.4 12 October 2002 (12.10.2002) GB

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): AVECIA LIMITED [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).

Published:

— with international search report

(72) Inventor; and

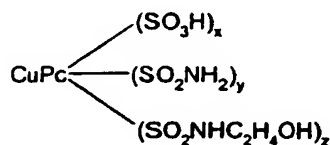
(75) Inventor/Applicant (*for US only*): PATEL, Prakash [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

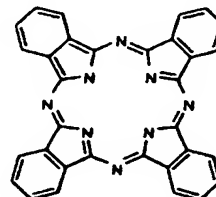


WO 2004/035700 A1

(54) Title: PHTHALOCYANINE COMPOUNDS USED IN INKS



(1)



(2)

(57) Abstract: Ink comprising a compound of Formula (1) and salts thereof; Formula (1) wherein: Pc represents a phthalocyanine nucleus of Formula (2); Formula (2) x is greater than 0 and less than 1.8; y and z are both greater than 0; and the sum of (x+y+z) is 2.4 to 4.5; and a liquid medium. Also an ink-jet printing process, a material printed with an ink of the invention and an ink jet printing cartridge containing an ink of the invention.

## PHTHALOCYANINE COMPOUNDS USED IN INKS

This invention relates to inks, to printing processes, to printed substrates and to ink-jet printer cartridges.

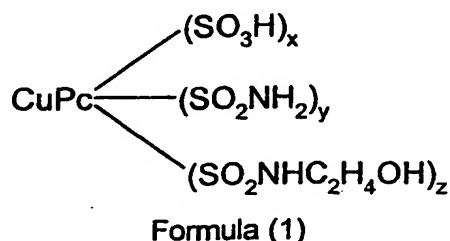
Ink-jet printing is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for inks used in ink-jet printing. For example they desirably provide sharp, non-feathered images having good water, light and ozone fastness with a good optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink-jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate that could block the printers fine nozzle.

Inks where the colorant is a dye containing a single copper phthalocyanine group such as, for example, C.I. Direct Blue 199 and C.I. Direct Blue 86 are known. Inks comprising newer phthalocyanines are also known, for example as described in US 6,149,722. However, there is a continuing need to provide inks having superior properties in ink-jet printing.

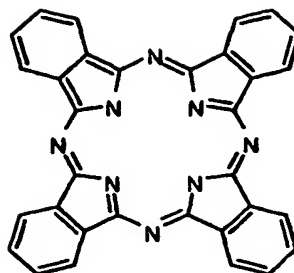
A particular problem for photorealistic quality printing is that of permanence, that is the ability of the colourants used in producing a photographic print to retain their colour properties over a number of years. A key factor contributing to the poor permanence of prints is the quenching of printed colorants by atmospheric pollutants, such as ozone.

According to the present invention there is provided an ink comprising a compound of Formula (1) and salts thereof:



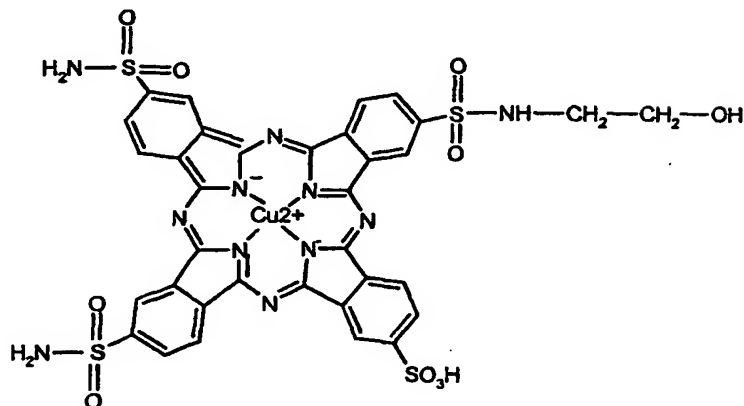
wherein:

Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

- 5           x is greater than 0 and less than 1.8;  
           y and z are both greater than 0; and  
           the sum of (x+y+z) is 2.4 to 4.5; and  
 provided that the compound of Formula (1) is not of formula



10

and a liquid medium.

- Preferably x is greater than 0 and less than 1.5, more preferably x is greater than 0 and less than 1.2, especially x is greater than 0.05 and less than 1.0, more especially x is greater than 0.05 and less than 0.8 and particularly x is greater than 0.05 and less than 0.5.

15

          Preferably the sum of y + z is in the range of from 2.4 to 4.2, more preferably 2.7 to 4.1.

          The sum of (x + y + z) is preferably 3.5 to 4.5, more preferably the sum of (x + y + z) is 3.8 to 4.2.

20

          The values for x, y and z in compounds of Formula (1) all represent statistical averages.

          Acid or basic groups on the compounds of Formula (1), particularly acid groups, are preferably in the form of a salt. Thus, the Formulae shown herein include the compounds in free acid and in salt form.

Preferred salts are alkali metal salts, especially lithium, sodium and potassium, ammonium and substituted ammonium salts (including quaternary amines such as  $((\text{CH}_3)_4\text{N}^+)$  and mixtures thereof. Especially preferred are salts with sodium, lithium, ammonia and volatile amines, more especially sodium salts. The compounds may be converted into a salt using known techniques.

The compounds of Formula (1) may exist in tautomeric forms other than those shown in this specification. These tautomers are included within the scope of the present invention.

The compounds of Formula (1) may be prepared by condensing copper phthalocyanine carrying sulphonyl chloride groups and optionally sulphonic acid groups with ammonia and ethanolamine. The condensation is preferably performed in water at a pH above 7. Typically the condensation is performed at a temperature of 30 to 70°C and the condensation is usually complete in less than 24 hours. Ammonia and ethanolamine may be used as a mixture or condensed sequentially with the phthalocyanine.

Copper phthalocyanine carrying sulphonyl chloride groups and optionally sulphonic acid groups may be prepared by chlorosulphonating copper phthalocyanine, e.g. using chlorosulphonic acid and optionally a chlorinating agent (e.g.  $\text{POCl}_3$ ,  $\text{PCl}_5$  or thionylchloride).

Preferred liquid media include water, a mixture of water and organic solvent and organic solvent free from water.

When the medium comprises a mixture of water and organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. Preferred water-miscible organic solvents include  $\text{C}_{1-6}$ -alkanols, preferably methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, *sec*-butanol, *tert*-butanol, *n*-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; ketones and ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and diacetone alcohol; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono- $\text{C}_{1-4}$ -alkyl ethers of diols, preferably mono- $\text{C}_{1-4}$ -alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, *N*-methyl-2-pyrrolidone, *N*-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone;

cyclic esters, preferably caprolactone; sulphoxides, preferably dimethyl sulphoxide and sulpholane. Preferably the liquid medium comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

5 Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl ethers of diols, more preferably mono- C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol.

10 Examples of further suitable liquid media comprising a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 4,251,50A.

15 When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents are any of the hereinbefore-described water-miscible organic solvents and mixtures thereof. Preferred water-immiscible solvents include, for example, aliphatic hydrocarbons; esters, preferably ethyl acetate; chlorinated hydrocarbons, preferably CH<sub>2</sub>Cl<sub>2</sub>; and ethers, preferably diethyl ether; and mixtures thereof.

20 When the liquid medium comprises a water-immiscible organic solvent, preferably a polar solvent is included because this enhances solubility of the compound in the liquid medium. Examples of polar solvents include C<sub>1-4</sub>-alcohols.

25 In view of the foregoing preferences it is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone) and/or an alcohol (especially a C<sub>1-4</sub>-alkanol, more especially ethanol or propanol).

30 The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected that gives good control over the drying characteristics and storage stability of the ink.

Liquid media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

35 The liquid media may also contain additional components conventionally used in ink-jet printing inks, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides, fogging reducing additives and surfactants which may be ionic or non-ionic.

Although not usually necessary, further colorants may be added to the ink to modify the shade and performance properties. Examples of such colorants include C.I.Direct Yellow 86, 132, 142 and 173; C.I.Direct Blue 199, and 307; C.I.Food Black 2; C.I.Direct Black 168 and 195; and C.I.Acid Yellow 23. Addition of such further dyes can increase overall solubility leading to less clogging (nozzle blockage) for the resultant ink.

Preferred inks comprise:

(a) from 0.01 to 30 parts of a compound of Formula (1); and

(b) from 70 to 99.99 parts of a liquid medium.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

Preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of liquid ink concentrates that may be used to prepare more dilute inks and reduces the chance of the dyestuffs in the precipitating if evaporation of the liquid medium occurs during storage.

Inks of the present invention are preferably prepared using high purity ingredients and/or by purifying the ink after it has been prepared. Suitable purification techniques are well known, e.g. ultrafiltration, reverse osmosis, ion exchange and combinations thereof (either before or after they are incorporated in a ink according to the present invention).

Preferably the ink has a viscosity of less than 20 cP, more preferably less than 10 cP, especially less than 5 cP, at 25°C. Low viscosity inks are particularly well suited for application to substrates by means of ink-jet printers.

Preferably the ink contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of divalent and trivalent metal ions (other than any divalent and trivalent metal ions bound to a component of the ink). Free divalent and trivalent metals can form insoluble complexes on storage that could block the ink-jet printer nozzles.

Preferably the ink has been filtered through a filter having a mean pore size below 10µm, more preferably below 3µm, especially below 2µm, more especially below 1µm. This filtration removes particulate matter that could otherwise block the fine nozzles found in many ink-jet printers.

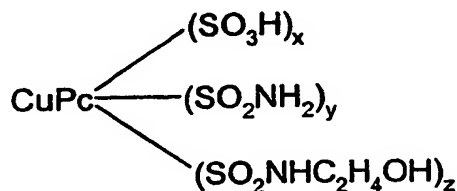
Preferably the ink contains less than 500ppm, more preferably less than 250ppm, especially less than 100ppm, more especially less than 10ppm in total of halide ions. High levels of halide ions can cause detrimental effects such as, for example, corrosion of metal parts in the ink-jet printer heads.

The inks of the present invention display excellent storage stability and provide prints which have attractive, strong cyan shades. In particular prints formed using these inks display excellent light and ozone fastness. Furthermore the colorant used in the inks,

that is compounds of Formula (1), may be prepared from cheap intermediates, avoiding the complexity and expense which is involved in manufacturing some of the more elaborate phthalocyanines.

A second aspect of the invention provides an ink comprising:

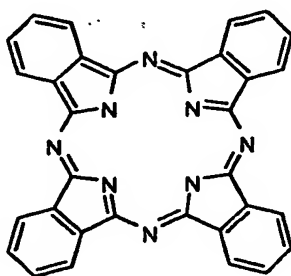
- 5 (a) a compound of Formula (1) and salts thereof:



Formula (1)

10 wherein:

Pc represents a phthalocyanine nucleus of Formula (2);



Formula (2)

x is greater than 0 and less than 1.8;

y and z are both greater than 0; and

the sum of (x+y+z) is 2.4 to 4.5; and

- 20 (b) a liquid medium which comprises a mixture of water and organic solvent or organic solvent free from water.

Preferences for the ink, compounds of Formula (1) and organic solvents are as described in the first aspect of the invention.

25 A third aspect of the invention provides a process for forming an image on a substrate comprising applying ink according to the first or second aspects of the invention thereto by means of an ink-jet printer.

30 The ink-jet printer preferably applies the ink to the substrate in the form of droplets that are ejected through a small orifice onto the substrate. Preferred ink-jet printers are piezoelectric ink-jet printers and thermal ink-jet printers. In thermal ink-jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor

adjacent to the orifice, thereby causing the ink to be ejected from the orifice in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink-jet printers the oscillation of a small crystal causes ejection of the ink from the orifice. Alternately the ink can be ejected by an electromechanical actuator connected to a moveable paddle or plunger, for example as described in International Patent Application WO 00/48938 and International Patent Application WO 00/55089.

The substrate is preferably paper, plastic, textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character.

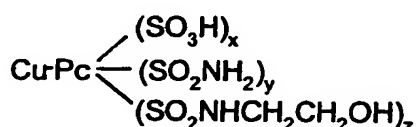
A fourth aspect of the present invention provides paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper more especially plain, coated or treated papers printed with ink according to the first or second aspects of the invention or by a process according to the third aspect of the invention.

A fifth aspect of the present invention provides an ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in the first or second aspects of the present invention.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

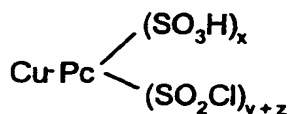
#### Example 1

Preparation of ink comprising the following dye wherein x is 0.8 and (y + z) is 3.2:



#### Stage 1

Preparation of:



Copper phthalocyanine (118.7g: molar ratio 1) was added in portions to a mixture of stirred chlorosulphonic acid (310 ml: molar ratio 23) and phosphorous oxychloride (37.8 ml: molar ratio 2) while keeping the temperature in the range of 50 to 60°C. The mixture was heated gradually to 140°C, and kept at that temperature, with stirring, for 3 hours.



The reaction mixture was then poured onto a mixture of ice (3kg), water (1400ml) and sodium chloride (160g). The precipitate which formed was collected by filtration at reduced pressure and washed with 3% brine (500 ml) before being used in Stage 2.

5     Stage 2

Preparation of the title dye:

      Water (2 litre), ethanolamine (24.6 g, molar ratio 2) and 35% ammonia solution (20g: molar ratio 2) were mixed in a 5 litre beaker and then placed in an ice bath (pH = 11.5, temperature 8°C). The phthalocyanine sulphonyl chloride paste (molar ratio 1),  
10     resulting from stage 1 above, was slowly added to the mixture while the temperature was kept below 5°C and the pH was maintained at pH 8 by the addition of 10% v/v sodium hydroxide. The reaction mixture was left overnight at room temperature and then heated at 40°C for 4 hours. Sodium chloride (50% w/v) was added and the resultant precipitate was collected by filtration at reduced pressure and desalinated by dialysis to obtain the  
15     title dye wherein x is 0.8 and (y + z) is 3.2.

Stage 3

Preparation of the ink:

      An ink of the present invention was prepared by dissolving 3.5g of the dye  
20     prepared in stage 2 in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Examples 2 to 9

Stage 1 and 2

25     Stage 1 and 2 of Example 1 was repeated except that the relative values of x, y and z in the dye in the ink were varied by changing the molar ratios of POCl<sub>3</sub>, ethanolamine and ammonia as shown in Table 1.

Stage 3

30     Inks were prepared from the dyes prepared in stage 2 as described in stage 3 of Example 1.

Examples 10 to 16

Stage 1

35     The method of Example 1, stage 1, was repeated except that the molar ratio of POCl<sub>3</sub> used in each example was as shown in Table 1.

Stage 2

Water (1 litre) and ethanolamine (12g, molar ratio 1) were mixed and then placed in an ice bath. The phthalocyanine sulphonyl chloride pastes (molar ratio 1), prepared as described in stage 1 were slowly added to the mixture while the temperature was kept below 5°C and the pH was maintained at pH 8 by the addition of 10% v/v. ammonia solution. The reaction mixture was left overnight at room temperature and then heated at 40°C for 4 hours. Sodium chloride (20% w/v) was added and the resultant precipitate was collected by filtration at reduced pressure and desalinated by dialysis to obtain the phthalocyanine dyes described in Examples 10 to 16 of Table 1 below.

Stage 3

Inks were prepared from the dyes prepared in stage 2 as described in stage 3 of Example 1.

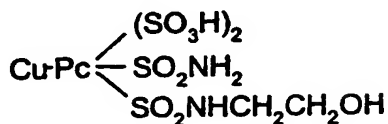
Table 1

Dye in Example	POCl <sub>3</sub> (molar ratio)	Ethanolamine (molar ratio)	Ammonia (molar ratio)	x	y + z
2	2	4	2	0.1	4.0
3	2	6	2	0.1	4.0
4	2	2	4	1.1	3.0
5	2	2	6	1.0	3.0
6	2.5	2	4	0.4	3.4
7	2.5	4	2	0.2	3.6
8	2.5	2	6	0.2	3.4
9	2.5	2	2	0.6	3.2
10	1.5	1	AR	1.3	2.8
11	2	1	AR	0.8	3.2
12	2.5	1	AR	1.4	2.6
13	3	1	AR	0.8	3.2
14	3.5	1	AR	0.4	3.6
15	3.8	1	AR	0.4	3.8
16	1	1	AR	0.7	3.4

AR – as required to adjust the pH is step (b) to pH 8.0.

Comparative ExampleStage 1Preparation of the comparative phthalocyanine dye:

The phthalocyanine dye wherein x is 2, y is 1 and z is 1:



was prepared as described in Example 1 of US 6,149,722 which preparation is incorporated herein by reference.

Stage 2Preparation of the comparative ink:

The compound prepared in stage 1 (3.5g) was dissolved in 100 ml of a liquid medium consisting of 2-pyrrolidone/thiodiglycol/Sufynol™ 465 in a weight ratio of 5:5:1.

Example 34Ozone Fastness

The Example Inks 1 to 16 and the Comparative Ink were printed onto a variety of papers using a Canon 5800™ IJ printer. The printed substrate was then assessed for ozone stability using an ozone test cabinet from Hampden Test Equipment. The test was carried out for twenty four hours at 40°C and 50% relative humidity in the presence of 1 part per million of ozone. Fastness of the printed ink to ozone was judged by the difference in the optical density before and after exposure to ozone using a Gretag MacBeth Spectrolino. Thus, the lower the %OD loss the greater the ozone fastness. Results are shown below in Table 2 and these clearly demonstrate that inks based on compounds of this invention display good ozone fastness.

Table 2

Example Ink	Substrate	% OD loss
Ink 1	HP Premium Plus	2
Ink 1	Canon PR101	48
Ink 1	SEC Premium Photo	53
Ink 2	HP Premium Plus	0
Ink 2	Canon PR101	27
Ink 2	SEC Premium Photo	21
Ink 3	HP Premium Plus	0

Ink 3	Canon PR101	27
Ink 3	SEC Premium Photo	12
Ink 4	HP Premium Plus	2
Ink 4	Canon PR101	53
Ink 4	SEC Premium Photo	54
Ink 5	HP Premium Plus	3
Ink 5	Canon PR101	52
Ink 5	SEC Premium Photo	45
Ink 6	HP Premium Plus	2
Ink 6	Canon PR101	39
Ink 6	SEC Premium Photo	38
Ink 7	HP Premium Plus	3
Ink 7	Canon PR101	30
Ink 7	SEC Premium Photo	28
Ink 8	HP Premium Plus	2
Ink 8	Canon PR101	33
Ink 8	SEC Premium Photo	33
Ink 9	HP Premium Plus	-1
Ink 9	Canon PR101	41
Ink 9	SEC Premium Photo	41
Ink 10	HP Premium Plus	2
Ink 10	Canon PR101	43
Ink 10	SEC Premium Photo	45
Ink 11	HP Premium Plus	1
Ink 11	Canon PR101	37
Ink 11	SEC Premium Photo	39
Ink 12	HP Premium Plus	4
Ink 12	Canon PR101	55
Ink 12	SEC Premium Photo	56
Ink 13	HP Premium Plus	3
Ink 13	Canon PR101	23
Ink 13	SEC Premium Photo	19
Ink 14	HP Premium Plus	0
Ink 14	Canon PR101	17
Ink 14	SEC Premium Photo	12
Ink 15	HP Premium Plus	1
Ink 15	Canon PR101	15

Ink 15	SEC Premium Photo	7
Ink 16	HP Premium Plus	2
Ink 16	Canon PR101	28
Ink 16	SEC Premium Photo	25
Comparative Ink	HP Premium Plus	4
Comparative Ink	Canon PR101	71
Comparative Ink	SEC Premium Photo	64

#### Further Inks

5 The inks described in Tables A and B may be prepared using the compounds made in Examples 1 to 16. Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink-jet printing.

The following abbreviations are used in Table A and B:

PG = propylene glycol  
 DEG = diethylene glycol  
 10 NMP = N-methyl pyrrolidone  
 DMK = dimethylketone  
 IPA = isopropanol  
 MEOH = methanol  
 2P = 2-pyrrolidone  
 15 MIBK = methylisobutyl ketone  
 P12 = propane-1,2-diol  
 BDL = butane-2,3-diol  
 CET = cetyl ammonium bromide  
 PHO = Na<sub>2</sub>HPO<sub>4</sub> and  
 20 TBT = tertiary butanol  
 TDG = thiodiglycol

TABLE A

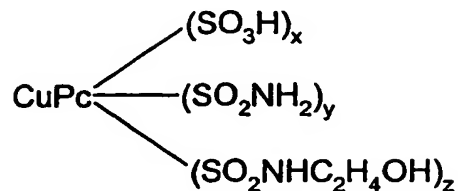
Dye of Example	Dye Content	Water	PG	DEG	NMP	DMK	NaOH	Na Stearate	IPA	MEOH	2P	MIBK
1	2.0	80	5		6	4					5	
2	3.0	90		5	5		0.2					
3	10.0	85	3		3	3				5	1	
4	2.1	91		8								1
5	3.1	86	5					0.2	4			5
6	1.1	81			9		0.5				9	
7	2.5	60	4	15	3	3			6	10	5	4
8	5	65		20					10			
9	2.4	75	5	4		5				6		5
10	4.1	80	3	5	2	10		0.3				
11	3.2	65		5	4	6			5	4	6	5
12	5.1	96								4		
13	10.8	90	5						5			
14	10.0	80	2	6	2	5			1		4	
15	1.8	80		5							15	
16	2.6	84			11						5	
14	3.3	80	2			10				2		6
15	12.0	90				7	0.3		3			
14	5.4	69	2	20	2	1					3	3
15	6.0	91			4						5	

TABLE B

Dye of Example	Dye Content	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P	PI2
1	3.0	80	15			0.2					5	
2	9.0	90		5						1.2		5
3	1.5	85	5	5		0.15	5.0	0.2				
4	2.5	90		6	4					0.12		
5	3.1	82	4	8		0.3						6
6	0.9	85		10					5	0.2		
7	8.0	90		5	5			0.3				
8	4.0	70		10	4				1			11
9	2.2	75	4	10	3				2		4	
10	10.0	91			6						6	
11	9.0	76			7		3.0			0.95	3	
12	5.0	78	5	9							5	
13	5.4	86		11	7						6	
14	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	7	
15	2.0	90		10							5	
16	2	88										
14	5	78			5			10				
15	8	70	2		8			12			5	
14	10	80						15			5	
15	10	80		10				8			12	

CLAIMS

1. An ink comprising a compound of Formula (1) and salts thereof:



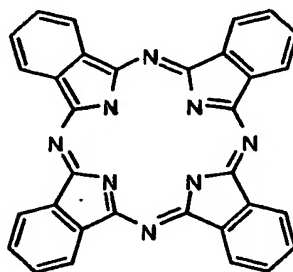
5

Formula (1)

wherein:

Pc represents a phthalocyanine nucleus of Formula (2);

10



Formula (2)

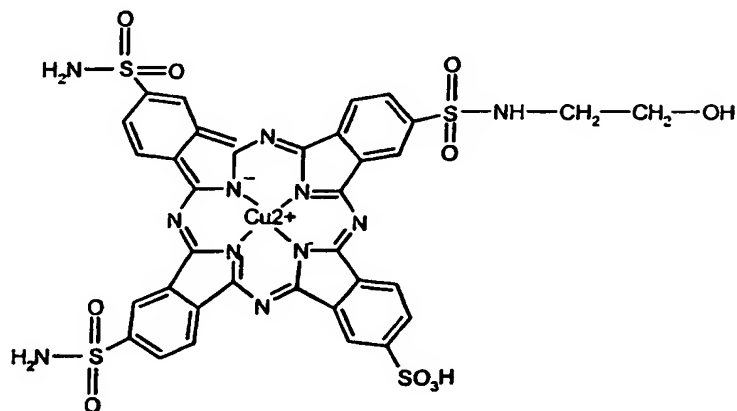
15

x is greater than 0 and less than 1.8;

y and z are both greater than 0; and

the sum of (x+y+z) is 2.4 to 4.5; and

provided that the compound of Formula (1) is not of formula

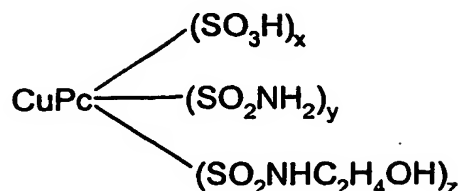


20

and a liquid medium.



2. An ink comprising:  
 (a) a compound of Formula (1) and salts thereof:

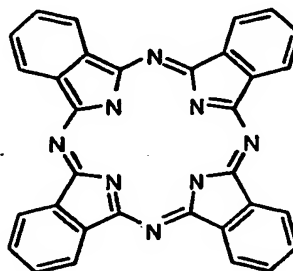


5

Formula (1)

wherein:

Pc represents a phthalocyanine nucleus of Formula (2);



10

Formula (2)

- 15 x is greater than 0 and less than 1.8;  
 y and z are both greater than 0; and  
 the sum of (x+y+z) is 2.4 to 4.5: and

(b) a liquid medium which comprises a mixture of water and organic solvent or organic solvent free from water.

- 20 3. An ink according to either claim 1 or claim 2 wherein x is greater than 0 and less than 1.5.
4. An ink according to any one of the preceding claims wherein x is greater than 0 and less than 1.2.
- 25 5. An ink according to any one of the preceding claims wherein x is greater than 0.05 and less than 1.0.
6. An ink according to any one of the preceding claims wherein x is greater than 0.05 and less than 0.5.
- 30

7. An ink according to any one of the preceding claims wherein  $y + z$  is in the range of from 2.4 to 4.2.

5 8. An ink according to any one of the preceding claims wherein  $y + z$  is in the range of from 2.7 to 4.1.

9. A process for forming an image on a substrate comprising applying an ink, according to any one of claims 1 to 8, thereto by means of an ink-jet printer.

10 10. A paper, plastic, textile, metal or glass material printed with an ink according to any one of claims 1 to 8.

11. An ink-jet printer cartridge comprising a chamber and an ink wherein the ink is in the chamber and the ink is as defined in any one of claims 1 to 8.

15

## INTERNATIONAL SEARCH REPORT

International Publication No

PCT/GB 03/04023

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C09D11/00 C09B47/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C09D C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99 67334 A (AVECIA LTD.) 29 December 1999 (1999-12-29) cited in the application page 6, line 25 -page 9, line 5; claims 1-6; example 1	1
A	EP 1 243 626 A (EASTMAN KODAK COMPANY) 25 September 2002 (2002-09-25) claims 1-7	1
A	WO 98 49240 A (ZENECA LTD.) 5 November 1998 (1998-11-05) claims 1-7	1
P, X	EP 1 254 932 A (HEWLETT-PACKARD COMPANY) 6 November 2002 (2002-11-06) the whole document	1-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

22 January 2004

Date of mailing of the international search report

30/01/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+31-70) 340-3016

Authorized officer

Permentier, W

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 03/04023

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9967334	A	29-12-1999	AT 247693 T	15-09-2003
			AU 4278999 A	10-01-2000
			CN 1116364 B	30-07-2003
			DE 69910581 D1	25-09-2003
			EP 1239010 A1	11-09-2002
			EP 1093492 A1	25-04-2001
			WO 9967334 A1	29-12-1999
			JP 2002522561 T	23-07-2002
			TW 538104 B	21-06-2003
			US 6149722 A	21-11-2000
EP 1243626	A	25-09-2002	US 2003000421 A1	02-01-2003
			EP 1243626 A1	25-09-2002
			JP 2002362004 A	18-12-2002
WO 9849240	A	05-11-1998	AU 6928498 A	24-11-1998
			DE 69808899 D1	28-11-2002
			EP 0975698 A1	02-02-2000
			WO 9849240 A1	05-11-1998
			JP 2001526649 T	18-12-2001
			US 2001011396 A1	09-08-2001
EP 1254932	A	06-11-2002	US 2003015120 A1	23-01-2003
			EP 1254932 A2	06-11-2002
			JP 2002371215 A	26-12-2002

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**